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(19)

(54) MODIFIED NEMATOGENIC COMPOSITIONS

(71) We, MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG of 250 Frankfurter Strasse, 61 Darmstadt, Germany, a Joint-Stock Company organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention is concerned with nematogenic compositions.

Nematogenic materials are used for the conversion of electrical voltage signals into optical signals. As a rule, for this purpose, a thin layer of liquid crystals is embedded between two electrical conductor coated glass plates, which act as electrodes. When an electrical voltage is applied to the two conductors, a microscopically visible, strong turbulence is produced in the nematic layer, together with a macroscopically visible, intensive increase of the light scattering of the electrode device. The system thereby becomes cloudy and opaque.

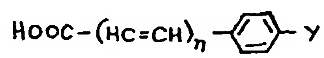
The great advantages of this kind of electro-optical device could first only be readily utilised when nematic phases had been found which were very stable in direct and alternating electrical currents and had a high chemical stability. In the meantime, a whole series of such nematogenic compositions have been described, especially those with very low melting and wide nematic mesophase ranges.

Normally, nematogenic compositions or compounds in a thin layer between glass or electrode plates form streaky and non-oriented layers which result in a reduced contrast of the indicator units and in a rather unattractive appearance. When present in the form of a thin layer between two glass plates or electrodes, the molecules of such materials have several possibilities of orientation. If all molecules are oriented with their longitudinal axes vertical to the electrode surfaces, then the indicator device appears, without the application of an electrical voltage, to be completely transparent at any angle of observation. If the molecule axes of the molecules constituting the nematogenic material all lie uniformly parallel to the glass surfaces, then the phase is transparent when observed at an angle of incidence of about 90°. However, at lower angles of incidence, layers of this kind have a slightly cloudy appearance. In the case of nematogenic material which contain azoxybenzene derivatives, this is especially disadvantageous because the inherent yellow colour of the azoxybenzene derivatives is, in the case of parallel orientation of the molecules, measurably more intense than in the case of vertical orientation. Furthermore, the preferred direction of the molecules may differ at different points of the nematic layer. In this case, the nematic phase shows, at any angle of incidence, a non-uniform, cloudy appearance with streaks passing therethrough.

Although, when used in a display unit, the orientation of the nematic phase between the electrodes is not of decisive importance, nevertheless, vertically oriented layers are always to be preferred because, upon the application of an electrical field, these provide, at any angle of incidence, substantially better contrasts with the regions to which a voltage is not applied than parallel or even non-homogeneously oriented nematic layers.

We have now found that nematogenic compositions or compounds can be modified in such a manner that they undergo orientation, without difficulty, to give stable, vertically oriented layers between plates, which plates can also be provided with conductive coatings.

Thus, according to the present invention, there is provided a nematogenic composition or compound which comprises a known nematogenic composition or compound containing 0.001—2% by weight and preferably 0.01 to 0.25% by weight, of at least one carboxylic acid of the general formula:—



(I)

[*Price 25p*]

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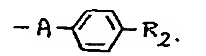
and/or at least one salt thereof, in which

Y is

$—R_1$

or



A is

—CH=CH—, —CX=CH—,

—CH=CX—, —C≡C—, —N=N—,

$—\underset{\downarrow \atop O}{N}=N—$, $—N=\underset{\downarrow \atop O}{N}—$, —O—CO—,

—CO—O—, —CH=N—, —N=CH—,

$—CH=\underset{\downarrow \atop O}{N}—$ or $—\underset{\downarrow \atop O}{N}=CH—$,

n is 0 or 1, R_1 is an alkyl or alkoxy radical containing 6 to 18 carbon atoms or an acyloxy radical containing 4 to 18 carbon atoms when *n* is 0, R_2 is an alkyl, alkoxy or acyloxy radical containing up to 18 carbon atoms, X is a halogen atom, preferably a chlorine atom, and $R_1=R_2$ when *n* is 1.

According to the present invention, there are preferably used those carboxylic acids of general formula (I) and/or their salts, the radical A of which has the same structure as is contained in the nematogenic compound or at least one of the substances forming the nematogenic composition.

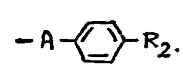
The present invention also provides a process for the modification of nematogenic compositions or compounds, wherein at least one carboxylic acid of general formula (I) and/or at least one salt thereof is added to a known nematogenic composition or compound in an amount of 0.001 to 2% by weight and preferably of 0.01 to 0.25% by weight.

Surprisingly, nematogenic composition which contain at least one carboxylic acid of general formula (I) and/or at least one salt thereof in the given amount, undergo orientation without difficulty and mostly spontaneously, to give vertically oriented layers in which the molecules of the nematogenic composition lie with their longitudinal axes vertical to the boundary surfaces of the display device.

The carboxylic acids of general formula (I) to be used according to the present invention are essentially characterised in that a carboxyl group is present in conjugation with a phenyl ring, which carries a long radical in the *p*-position. Further substituents on this phenyl ring, especially those which can sterically hinder the carboxyl group, are, as a rule, undesirable but smaller radicals in the *o*- or *m*-position to the carboxyl group normally do not have a disturbing effect, particularly when the radical Y is an especially long radical. It must, however, be ensured that the carboxyl group can react with the surface of the display device, which surface can be provided with a conductive coating.

It is important that the carboxylic acids and/or their salts used according to the present invention possess a sufficient degree of solubility in the nematogenic composition or compound to be modified. Since, however, only very small amounts of the acids and/or salts are necessary in order to achieve the desired effect, this condition of sufficient solubility is, as a rule, fulfilled. Carboxylic acids and salts are preferred in which Y is a long radical. The alkyl, alkoxy and acyloxy radicals can contain up to 18 carbon atoms, non-branched radicals being preferred.

The carboxylic acids of general formula (I) which bring about the vertical orientation are either benzoic acids substituted in the *p*-position or carboxy derivatives of substituted azobenzenes, of azoxybenzenes, of Schiff bases (especially benzylidene derivatives), of stilbenes, especially of *trans*-stilbenes, of phenyl benzoates, of diphenyl-acetylenes, of diphenyl nitrones or of cinnamic acids which are substituted in the p-position by R_1 *or*



Insofar as Y is an alkyl radical, unbranched radicals, such as *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-dodecyl and the higher homologues containing up to 18 carbon atoms, are preferred. Amongst the alkoxy radicals may be mentioned the hexyloxy, octyloxy and dodecyloxy radicals, because of the ready accessibility of the starting materials, although all other homologues containing up to 18 carbon atoms can also be used. The acyloxy radicals R_1 are also preferably unbranched radicals containing 4—18 carbon atoms, for example, butyryloxy, valeryloxy, capronyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, dodecanoyloxy and the higher homologues containing up to 18 carbon atoms.

These radicals can also be used as substituents R_2 but, in this case, the lower homologues are also to be included. Thus, alkyl radicals R_2 include not only those mentioned above but also methyl, ethyl, propyl, *n*-butyl and *n*-pentyl radicals, the corresponding alkoxy radicals also include methoxy, ethoxy and propoxy radicals and for the acyloxy radicals also include acetoxy and propionoxy radicals.

The carboxylic acids of general formula (I), some of which are new compounds, can be prepared in various ways according to the standard processes described in the literature.

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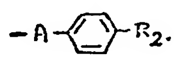
Thus, for example, all compounds of general formula (I) which, instead of a carboxyl group, contain a substituent convertible into a carboxyl group, can be converted by known processes into the corresponding carboxylic acids. The preferred substituents are those which are able to provide carboxyl groups solvolytically, especialyl hydrolytically, or oxidatively. Because of the ready accessibility of the starting materials, there are preferably used nitriles, esters and carboxylic acid amides which, in each case, can be saponified by hydrolysis to give carboxylic acids of general formula (I). A further possibility is the oxidation of phenones, for examples with hydrogen peroxide in glacial acetic acid, followed by hydrolysis. These proceses are also sufficiently described in and known from the literature.

The carboxylic acids of general formula (I), in which Y is the radical

are preferably prepared by joining two fragments, each of which introduces a phenyl ring into the molecule. In this way, there can readily be prepared all compounds of general formula (I) in which Y is the radical



with the exception of the compounds in which A is —C≡C—. A subsequent reaction is here still necessasry.

The connecting of the two aromatic radicals with functional groups can be carried out, for example, by a Wittig reaction, in which, as is known, from alkylidene and arylidene phosphoranes and carbonyl compounds, the corresponding olefins result, i.e. in this case, stilbenes of general formula (I), wherein A is —CH=CH—. By bromination of these stilbenes and subsequent splitting off of hydrogen bromide, it is easy to obtain, according to known methods, the diphenyl - acetylene - carboxylic acids of general formula (I) in which A is —C≡C—.

The azo and azoxy compounds of general formula (I) can also easily be obtained by known coupling reactions. Thus, according to standard methods, nitroso compounds and amines can be reacted to give azo compounds and nitroso compounds and hydroxylamine derivatives can be reacted to give the corresponding azoxy compounds. Azoxy compounds

$$A = -\underset{O}{\underbrace{N=N}}-$$

can also be obtained very easily from the corresponding azo compounds by oxidation with, for example, hydrogen peroxide.

For the preparation of phenyl benzoates of general formula (I)

(A= —CO—O— or —OCO—),

normal esterification conditions are chosen so that, for example, *p*-hydroxybenzoic acid can be reacted with a benzoic acid *p*-substituted by R_2 or with a functional derivative thereof or terephthalic acid or a functional derivative thereof is reacted with a phenol *p*-substituted by R_2.

The benzylidene derivatives of general formula (I) can be obtained by the reaction of appropriately substituted benzaldehydes with appropriately substituted anilines. Here, too, there can be used the standard methods for the formation of Schiff bases which are adequately described in the literature.

The cinnamic acids can be prepared in known manner by the condensation of benzaldehydes substituted by Y with malonic acid or acetic anhydride, whereas the corresponding nitrones are obtainable by condensation of phenylhydroxylamines substituted by R_2 with *p* - formyl - benzoic acid.

The compounds of general formula (I) can also be obtained by introducing a carboxyl group into compounds which, instead of a carboxyl group, contain an alkli metal atom, preferably lithium or an alkaline earth metal atom, for example magnesium (preferably prepared as the Grignard reagent from the corresponding halogen compound, for example, the bromine compound). These organometallic compounds can be reacted with carbon dioxide (for example under pressure or in the form of "dry ice") or with agents giving off carbon dioxide, for example chloroformic acid esters. In each case, the free acid is subsequently obtained by hydrolysis.

Finally, the introduction of the radical R_2 can also be carried out, for example, when a hydroxyl group present in the desired position is converted into an alkoxy or acyloxy radical.

From the various methods of synthesis available, it is clearly not difficult to select the simplest mode of preparation for a particular carboxylic acid of general formula (I), the availability of the starting materials being of decisive importance. The reaction conditions used are well-known from the appropriate chemical literature.

In many cases, it is also advantageous to use, at least in part, salts instead of the acids of general formula (I). Simultaneously with the vertical orientation, there is thereby obtained a modification of the conductivity so that the specific electrical resistance necessary for good reproducibility of the dynamic scattering effect can be adjusted. All salts can be

used, the deposition potential of which is lower than the field strengths in the nematic system. Large, space-filling cations are preferred.

In principle, all salts can be used which possess a sufficient degree of solubility in the nematogenic compositions or compounds and which do not provide protons. In addition to the alkali metal salts (sodium, potassium, lithium, rubidium and caesium) and the alkaline earth metal salts (calcium, strontium and barium), there can also be used, in particular, the ammonium and/or phosphonium salts. In these cations, all the ligands must be occupied by organic radicals and preferably by alkyl or phenyl radicals, since free hydrogen ions would have a disturbing effect in the intended field of use. Examples of preferred substituents in these ammonium and/or phosphonium cations include, in particular, straight or branched alkyl radicals containing up to 18 carbon atoms and phenyl radicals. Quaternary amonium compounds with the most varied alkyl radicals are available in large quantities because they are extensively used, for example, in the detergent industry. Amongst the phosphonium salts, the best known are those obtainable from triphenyl-phosphine or trialkyl-phosphines by reaction with alkyl halides.

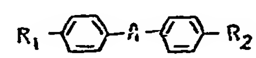
By way of example, the following ammonium cations may be mentioned: tetramethyl-ammonium, tetraethyl-amonium, tetrapropyl-ammmonium, tetrambutyl-ammonium, tetrapentyl-ammonium, tetrahexyl-ammonium, tetraheptyl-ammonium, tributyl - propyl - ammonium, triethyl - methyl - ammonium, triethyl - propyl - ammonium, trimethyl - phenyl - ammonium, cetyl - trimethyl - ammonium, octadecyl - trimethyl - ammonium and tetraphenyl-ammonium.

Readily obtainable phosphonium cations include, for example, the following: tetraphenyl-phosphonium, triphenyl - isopropyl - phosphonium, trioctyl - hexyl - phosphonium, tributyl - dodecyl - phosphonium and tributyl - octadecyl - phosphonium.

The preparation of the salts of the carboxylic acids of general formula (I) is also carried out in known manner. From the quaternary ammonium and phosphonium compounds used as starting material, which, as a rule, are in the form of halides, for example of bromides or chlorides, there are usually prepared the free bases with the help of ion exchanges. An alcoholic solution of these bases is then mixed with equimolar amounts of a carboxylic acid of general formula (I), which is also dissolved in an alcohol. After the evaporation of the solution and addition of ether, the salts precipitates out and can be added to the nematic phases in this form.

As nematogenic compositions, there can be used, according to the present invention, all mixtures which have, because of their liquid crystalline properties, hitherto been employed in electro-optical indicator devices or which are suitable for this purpose. The most commonly used compositions consist of mixtures of derivatives of the azobenzenes, azoxybenzenes, Schiff bases, especially benzylidene derivatives, phenyl benzoates, optionally halogenated stilbenes, diphenyl-acetylenes, diphenyl-nitrones and substituted cinnamic acids. In general, isomeric pairs and/or eutectic mixtures are used.

The most important components of the known nematogenic compositions can be represented by the general formula:—



(II)

wherein A has the same meaning as in general formula (I) and R_1 and R_2, which may be the same or different, are alkyl, alkoxy or acyloxy radicals which contain up to 18 and preferably up to 8 carbon atoms. In most of these compounds, R_1 and R_2 are preferably different, one of them usually being an alkyl radical and the other usually being an alkoxy or acyloxy radical. However, all other variants of the substituents can also be used. A large series of such nematogenic compositions is commercially available.

The nematogenic compositions or compounds are frequently modified by the addition of cholesterol compounds, in order to achieve memory effects. Such cholesterol compounds are generally used in amounts of about 10% by weight. A large number of nematic phases is described, for example, in German Patent Specification No. 1,951,092 and in British Patent Specifications Nos. 1,285,388; 1,346,874 and 1,350,369.

Solutions of acids of general formula (I) or of their salts in nematogenic compositions or compounds are characterised in that, when introduced between two boundary surfaces, they can form completely transparent layers, in which the longitudinal axes of the molecules are vertical to the boundary surfaces, i.e. they behave homotropically. The orienting action of the acids of general formula (I) is, surprisingly, not limited to nematogenic compositions or compounds of similar structure but is of general utility; it is merely a prerequisite that the acids and/or their salts have a sufficient degree of solubility in the nematogenic materials. Of course, the solubility is the better, the more closely related are the acids or their salts with the liquid crystals in their chemical structure. Since, however, even extraordinarily small amounts are sufficient for the achievement of the desired effect, the degree of solubility scarcely represents a limiting factor.

Furthermore, it is normally desirable not to

use the salts of general formula (I) alone but rather in admixture with the free carboxylic acids. The mixing ratio can be selected as desired.

The boundary surfaces between which the nematogenic compositions according to the present invention are to be introduced should be hydrophilic since, presumably, some reaction takes place between the carboxyl function and the surface. Thus, glass plates are especially well suited, as well as synthetic resins having hydrophilic groups on their surface, for example, polysaccharide materials, especially cellulose derivatives, for example celluloid. Furthermore, surfaces provided wholly or partially with conductive layers can be used as boundary surfaces. The most usual coatings of this type are of tin dioxide, which can be applied, for example, by reaction coating: however, other materials can also be employed, for example, indium oxide or tin oxide with antimony trioxide or mixtures of these materials. As is known, these conductive layers are frequently partially removed by etching so that patterns are formed which can be made visible by nematic liquid crystals. The dynamic scattering only occurs at those places at which two conductive layers lie opposite to one another. As a rule, the layer thickness of the nematogenic materials between the boundary surfaces is 5—40 microns but this range is not limiting. The display devices themselves, their construction and their dimensions are well known.

The oriented layers can be produced, for example, either by heating the nematogenic compositions to a temperature above the clear point, between an appropriate plate arrangement and then allowing to cool or by filling the boundary surface arrangement at ambient temperature and subsequently briefly heating to a temperature which lies at least a few degrees above the clear point of the nematogenic composition employed. In both cases, after cooling to ambient temperature, thermodynamically stable, vertically oriented layers are obtained.

Surprisingly, the tendency of these nematogenic compositions to form vertically oriented layers is so great that, with a content of $>0.01\%$ by weight of an acid of general formula (I) and/or a salt thereof, even after filling the plate arrangement at ambient temperature, they behave homotropically so that a subsequent warming above the clear point can be omitted. This process is preferably to be used when the boundary surfaces are uniform, i.e. when pure glass surfaces are used or no pattern has been etched on to the conductive coatings or in the case of very clean heterogeneous surfaces.

The nematogenic compositions according to the present invention can be used in the same way as the previously employed phases, i.e. especially for display systems. They can be used for example, for the digital indication of measurement data, of the results of electronic calculators, of the time of day or of process data or of numbers, letters or other symbols.

The modification of the nematogenic compositions or compounds according to the present invention is of especial advantage for nematogenic compositions or compounds based upon azoxy derivatives since the yellow colour of the indicator devices produced with such liquid crystals is considerably reduced. After the orientation, all transitional dipole moments of the azoxy chromophores stand vertically to the light vector of the incident lightwaves.

Surprisingly, a tendency for undesirable gas bubble formation in the nematogenic compositions according to the present invention is also considerably reduced. The period of life of a display system containing the modified nematogenic compositions or compounds is, therefore, considerably lengthened.

The following Examples are given for the purpose of illustrating the present invention:

Example 1.

5 g. of a eutectic mixture, melting at $-5°$ C., of *p* - (*n* - butoxy - *p'* - methoxy - azoxybenzene and *p* - ethyl - *p'* - methoxy - azoxybenzene are mixed with 12 mg. *p* - (*p* - methoxy - phenylazoxy) - benzoic acid (m.p. 207° C.). A drop of this solution, heated to 80—100°C., is applied to a 50 cm² rectangular glass plate which is provided with a conductive layer of tin dioxide and also heated to 80—100°C. On two composite edges of the glass plate, there are applied approximately 15 μ thick distance pieces made of synthetic resin film. A second glass plate of the same size, which has also been heated to about 80—100°C., is placed upon the first plate in such a manner that the conductive layers of the two plates face one another. The modified nematic phase thereby spreads out uniformly in the form of a thin layer between the two plates. After cooling, a nematic layer is obtained which, at ambient temperature, is completely vertically oriented. After sealing, it provides clear contrasts when used as a display device.

The electrode device can also be filled at ambient temperature and the solution also need not be previously heated. Under these conditions, too, vertically oriented, clear nematic layers are obtained.

The same result is obtained when, as carboxylic acid, there is used one or more of the following compounds: *p* - (*p* - ethoxyphenylazoxy) - benzoic acid, *p* - (*p* - hexyloxyphenylazoxy) - benzoic acid, *p* - (*p* - dodecyloxyphenylazoxy) - benzoic acid, *p* - (*p* - octadecyloxyphenylazoxy) - benzoic acid, *p* - (*p* - butrylyloxyphenylazoxy) - benzoic acid, *p* - (*p* - octanoyloxyphenylazoxy) - benzoic acid, *p* - (*p* - hexadecanoyloxyphenylazoxy) - ben-

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zoic acid, p - (p - n - hexylphenylazoxy) - benzoic acid or p - (p - tetradecylphenylazoxy) - benzoic acid.

Example 2.

5 g. of the eutectic mixture described in Example 1 are mixed with 5 mg. p - (p - hexyloxybenzoyloxy) - benzoic acid (m.p. 236°C.). A drop of the so obtained solution is applied at ambient temperature to a glass plate (or to a synthetic resin plate) coated with a conductive layer of tin dioxide. With the help of foil spacers, layer thicknesses of 6 to 30 μ are obtained. After applying a covering plate, which is also coated with tin dioxide, there are obtained vertically oriented layers which do not appear to be turbid at any angle of observation.

The same result is achieved when, as carboxylic acid, there is used one or more of the following compounds: (p - decyloxybenzoyloxy) - benzoic acid. (p - tetradecyloxybenzoyloxy) - benzoic acid, (p - butyryloxybenzoyloxy) - benzoic acid, (p - capronyloxybenzoyloxy) - benzoic acid, (p - octadecanoyloxybenzoyloxy) - benzoic acid, (p - butylbenzoyloxy) - benzoic acid, (p - octylbenzoyloxy) - benzoic acid or (p - octadecylbenzoyloxy) - benzoic acid.

Example 3.

In 1000 g. of the eutectic mixture according to Example 1, melting at −5°C., are dissolved 2.5 g p-hexoylbenzoic acid (m.p. 109°C., clear point 152°C.), as well as 50 mg. N - ethyl - N - dodecyl - N,N - dimethyl - ammonium - p' - hexyloxybenzoate. This solution has a specific electrical resistance of $4 . 10^{-9}$ Ωcm., which gives the optimum conductivity for the dynamic scattering effect.

Two approximately 50 cm² rectangular glass plates, at least one side of which has a conductive layer of tin dioxide, are laid upon one another so that the conductive layers are facing one another. Glass distance pieces are provided on two opposite sides of the plates so that, between the glass plates, a hollow space of 25 μ thickness is formed.

A drop of the above-mentioned solution, heated to 85°C., is introduced into one of two lateral openings of the electrode device, which is also heated to about 85°C. The nematic liquid spreads out uniformly in the hollow space due to capillary forces. After cooling to a temperature below 75°C. (i.e. to a temperature below the clear point of the nematic phase employed), a completely vertical oriented, glass-clear nematic layer is obtained which is stable at ambient temperature.

The same result is achieved when, as carboxylic acid, there is used one or more of the following compounds: p-nonyloxybenzoic acid (m.p. 97°C.; clear point 142°C.); p-decylbenzoic acid (m.p. 95°C.; clear point 139°C.); p-dodecyloxybenzoic acid (m.p. 88°C.; clear point 134°C.); p-tetradecyloxybenzoic acid (m.p. 81°C.; clear point 130°C.); p-hexadecyloxybenzoic acid (m.p. 94°C.; clear point 128°C.); p-butyryloxybenzoic acid; p-octadecanoyloxybenzoic acid; p-hexylbenzoic acid (m.p. 94°C.; clear point 103°C.); or p-dodecylbenzoic acid.

Example 4.

In 1000 g. of the eutectic mixture described in Example 1 are dissolved 200 mg. p - (p - hexyloxy - phenylazoxy) - benzoic acid.

A sandwich cell, heated to 80°C., which comprises two rectangular, about 8 cm² glass plates lying opposite one another, between which lie, on two opopsite sides, two 1.5 mm. wide, 20 μ thick distance pieces made of polyester foil, is brought into contact on one of the two lateral openings, with a drop, also heated to 80°C., of the above-described solution. Due to capillary forces, the liquid spreads out uniformly between the two glass plates and, after cooling to below 75°C., forms a homotropically oriented layer which is stable at ambient temperature.

The sandwich cell can also be filled at ambient temperature, in which case it is also unnecessary to warm the solution. In this case, too, uniformly transparent and vertically oriented nematic layers can be obtained.

Example 5.

In 1.5 kg. of the eutectic mixture, melting at −9°C., of the two isomer pairs p - (n - butyl) - p' - methoxy - azoxybenzene and p - ethyl - p' - valeryloxy - azoxybenzene, are dissolved 200 mg. 4' - hexyloxy - *trans* - stilbene - 4 - carboxylic acid.

With the use of this solution, there are produced vertically oriented nematic layers by the methods described in Examples 1—4.

The same result is achieved when, as carboxylic acid, there is used one or more of the following compounds: 4' - octyloxy - *trans* - stilbene - 4 - carboxylic acid, 4' - octadecyloxy - *trans* - stilbene - 4 - carboxylic acid, 4' - heptanoyloxy - *trans* - stilbene - 4 - carboxylic acid or 4' - decanoyl - *trans* - stilbene - 4 - carboxylic acid.

Example 6.

In 10 g. of the eutectic mixture, melting at −15°C., of p,p' - di - (n - butyl) - azoxybenzene and the isomer pair p - (n - butyl) - p' - methoxyazoxybenzene, are dissolved 4 mg. p - (p - ethoxy - phenylazoxy) - benzoic acid or p - (p - methoxy - phenylazoxy) - benzoic acid. With the use of this solution, there are produced vertically oriented nematic layers by the methods described in Examples 1—4.

Example 7.

In 5 g. of the isomer mixture, melting at 16°C., of p - (n - butyl) - p' - methoxy-

azoxybenzene, are dissolved 10 mg. *p* - (*p* - methoxyphenylazoxy) - benzoic acid (m.p. 209—210°C.). This solution is diluted with 5 g. *p,p'* - di - (*n* - butyl) - azoxybenzene so that a eutectic mixture is obtained melting at −15°C., which can be used with advantage for the production of vertically oriented, thin nematic layers by the methods described in Examples 1 to 4.

Example 8.

To 10 g. of the eutectic mixture, melting at −15°C., of *p,p'* - di - (*n* - butyl) - azoxybenzene and the isomer mixture of *p* - (*n* - butyl) - *p'* - methoxyazoxybenzene, are added 2 mg. 4 - (4 - butyloxybenzoyloxy) - benzoic acid. This mixture readily undergoes vertical orientation in thin layers. It can be introduced into display devices in a manner analogous to the methods described in Examples 1 to 4.

Example 9.

In 10 g. of a eutectic mixture, melting at −22°C., of *p* - (*n* - butyl) - benzoic acid *p*-hexyloxyphenyl ester, *p* - (*n* - hexyloxy) - benzoic acid *p* - (*n* - butyl) - phenyl ester, p-butrylyloxybenzoic acid *p* - (*n* - hexyloxy) - phenyl ester and *p*-butyryloxy benzoic acid *p*-methoxyphenyl ester, are dissolved 2 mg. *p* - (*p* - heptyloxybenzoyloxy) - benzoic acid. This solution is used, according to the methods described in Examples 1 to 4, for the production of vertically oriented, thin nematic layers.

Example 10.

To 100 g. of the eutectic nematic mixture, liquid at ambient temperature, of 25% *p* - (*p* - *n* - butylbenzoyloxy) - benzoic acid *p* - butyl - phenyl ester, 25% *p*-anisoyloxybenzoic acid *p*-butylphenyl ester, 30% *p*-methoxybenzoic acid *p*-butylphenyl ester and 20% *p* - (*p* - *n* - butylbenzoyloxy) - benzoic acid *p*-methoxyphenyl ester, are added 15 mg. *p* - (*p* - *n* - butylbenzoyloxy) - benzoic acid.

With the use of this solution, there are produced vertically oriented nematic layers by the methods described in Examples 1 to 4.

Example 11.

To 5 g. of the eutectic mixture, melting at 0°C., of *p* - (*n* - butyl) - benzoic acid *p*-hexyloxyphenyl ester and *p*-hexyloxybenzoic acid *p*-butylphenyl ester, are added 0.8 mg. 4' - butoxydiphenyl - acetylene - 4 - carboxylic acid. The mixture thus obtained undergoes orientation in this layers when it is worked up analogously to the methods described in Examples 1 to 4.

The same results are also achieved when using 4' - heptyloxy - diphenyl - acetylene - 4 - carboxylic acid or 4' - dodecyloxy - diphenyl - acetylene - 4 - carboxylic acid.

Example 12.

To 100 g. of a 1:1 mixture of N - (*p* - methoxybenzylidene) - *p* - (*n* - butyl) - aniline and N - (*p* - ethoxybenzylidene) - *p* - (*n* - butyl) - aniline are added 50 mg. *p* - (*p* - methoxybenzoyloxy) - benzoic acid. With the use of this solution, there are produced vertically oriented nematic layers by the methods described in Examples 1 to 4.

The same results are achieved when, as acid, there is used 50 mg. *p* - (*p* - hexyloxybenzoyloxy) - benzoic acid (m.p. 161°C.; clear point 235°C.).

Example 13.

To 10 g. of the eutectic mixture, melting at −3°C., of N - (*p* - methoxybenzylidene) - *p* - (*n* - butyl) - aniline, N - (*p* - methoxybenzylidene) - *p* - butyryloxyaniline and *p*-hexanoyloxy-benzoic acid *p*-ethoxyphenyl ester, are added 8 mg. *p*-hexanoyloxybenzoic acid (m.p. 152°C.). From this mixture are produced vertically oriented nematic thin layers in a manenr analogous to that described in Examples 1 to 4.

Example 14.

In 100 g. of the isomer mixture, melting at +16°C., of *p* - (*n* - butyl) - *p'* - methoxyazoxybenzene, are dissolved 6 mg. tetraphenyl - phosphonium - *p* - (*p'* - hexyloxyphenylazoxy) - benzoate and 100 mg. *p* - (*p* - hexyloxyphenylazoxy) - benzoic acid. This solution has a specific electrical resistance of 3 . 10^{-9} Ωcm. which gives the optimum conductivity for a successful application of the dynamic scattering effect and, additionally, has the property, when introduced into indicator devices with etched tin dioxide layers analogously to Example 3, of forming vertically oriented thin layers.

Example 15.

In a mixture of 9 g. of the eutectic mixture, melting at −22°C., of *p* - (*n* - butyl) - benzoic acid *p'*hexyloxyphenyl ester, *p* - (*n* - hexyloxy) - benzoic acid *p'* - (*n* - butyl) - phenyl ester, *p*-butyryloxybenzoic acid *p'*-hexyloxyphenyl ester and *p*-butyryloxybenzoic acid *p'*-methoxyphenyl ester, as well as of 0.5 g. cholesterol oleyl carbonate and 0.5 g. cholesterol nonanoate, are dissolved 5 mg. 4 - hexanoyloxy - benzoic acid. Upon working up analogously to Example 1, this solution provides vertically oriented layers.

Example 16.

10 g. of a mixture of 66% by weight *d,l* - 4 - (2 - methylhexyl) - 4' - ethoxy - α - chloro - *trans* - stilbene and 34% by weight 4 - (*n* - heptyl) - 4' - ethoxy - α - chloro - *trans* - stilbene are mixed with 4 mg. *p* - (*p* - butoxy - *trans* - stilbene) - carboxylic acid. When used analogously to Example 1, 2 or 3, this mixture provides homotropic, thin layers.

Example 17.

In 1 g. of a mixture of 65% by weight N - (*p* - methoxyphenyl) - α - (*p* - hexyloxyphenyl) - nitrone and 35% by weight N - (*p* - methoxyphenyl) - α - (*p* - *n* - heptylphenyl) - nitrone, is dissolved 0.5 mg N - (*p* - ethoxyphenyl) - α - *p* - phenyl - nitrone - carboxylic acid. This mixture forms vertically oriented layers in display devices.

Example 18.

In 1000 g. of the nematic phase described in Example 6 are dissolved 400 mg. (*p* - (*n* - hexyloxy) - cinnamic acid (m.p. 151°C., clear point 176°C.). This solution gives clear, vertically oriented layers when it is introduced into display devices analogously to Example 1, 2 or 3.

The same result is achieved when there is added one or more of the following carboxylic acids: *p* - (*n* - dodecyloxy) - cinnamic acid, *p* - (*n* - octadecyloxy) - cinnamic acid, *p* - cetyl - cinnamic acid, *p* - acetoxy - cinnamic acid, *p* - decanoyloxy - cinnamic acid, *p* - octadecanoyloxy - cinamic acid, *p* - (*p* - butoxyphenylazoxy) - cinnamic acid or *p* - (*p* - ethoxybenzoyloxy) - cinnamic acid.

Example 19.

In 100 g. of the nematic phase described in Example 6 are dissolved 35 mg. *p* - (*p* - pentyloxy - phenylazoxy) - benzoic acid. This solution gives clear, vertically oriented layers when it is introduced into display devices analogously to Examples 1, 2 or 3.

The same result is achieved when there is added one or more of the following carboxylic acids: *p* - (*p* - methoxy - phenylazo) - benzoic acid (m.p. 239°C.), *p* - (*p* - hexyloxy - phenylazo) - benzoic acid, p - (*p* - dodecyloxy - phenylazo) - benzoic acid, *p* - (*p* - octadecyl-oxy - phenylazo) - benzoic acid, *p* - (*p* - butyryloxy - phenylazo) - benzoic acid, *p* - (*p* - octanoyloxy - phenylazo) - benzoic acid, *p* - (*p* - hexadecanoyloxy - phenylazo) - benzoic acid, *p* - (*p* - hexyl - phenylazo) - benzoic acid, *p* - (*p* - decyl - phenylazo) - benzoic acid or *p* - (*p* - tetradecyl - phenylazo) - benzoic acid.

Example 20.

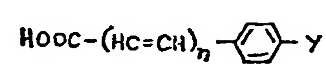
In 500 g. of a mixture of 50% *p* - methoxy - benzylidene - *p'* - (*n* - butyl) - aniline and 50% *p* - ethoxy - benzylidene - *p'* - (*n* - butyl) - aniline, are dissolved 200 mg. N - (*p* - methoxybenzylidene) - *p'* - aminobenzoic acid. This solution gives clear, vertically oriented layers when it is introduced into display devices analogously to Examples 1, 2 or 3.

Example 21.

In 50 g. of the nematic phase described in Example 1 are dissolved 40 mg. *p* - (*p* - methoxy - phenylazoxy) - benzoic acid and 25 mg. N - ethyl - N - dodecyl - N,N - dimethyl - ammonium - *p'* - hexyloxybenzoate. After incorporation into a display device at ambient temperature in a manner analogous to that described in Example 1, there is obtained a clear, homotropic nematic layer with a specific resistance of 5 . 10^{-9} Ωcm.

WHAT WE CLAIM IS: —

1. A nematogenic composition, comprising a known nematogenic composition or compound containing 0.001 to 2% by weight of at least one carboxylic acid of the general formula: —



and/or at least one salt thereof, in which

Y is

—R_1

or

A is

—CH=CH—, —XC=CH—,

—HC=CX, —C≡C—, —N=N—,

$\underset{\underset{O}{\downarrow}}{-N{=}N-}$, $\underset{\underset{O}{\downarrow}}{-N{=}N-}$, —O—CO—,

—CO—O—, —CH=N—, —N=CH—,

$\underset{\underset{O}{\downarrow}}{-CH{=}N-}$ or $\underset{\underset{O}{\downarrow}}{-N{=}CH-}$

n is 0 or 1, R_1 is an alkyl or alkoxy radical containing 6 to 18 carbon atoms or an acyloxy radical containing 4 to 18 carbon atoms when *n* is 0, R_2 is an alkyl, alkoxy or acyloxy radical containing up to 18 carbon atoms, X is a halogen atom and $R_1{=}R_2$ when *n* is 1.

2. A composition according to claim 1, wherein the acid and/or salt is present in an amount of 0.01 to 0.25% by weight.

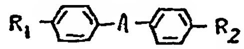
3. A composition according to claim 1 or 2, wherein the halogen atom X is a chlorine atom.

4. A composition according to any of the preceding claims, wherein the radical A of the carboxylic acid is also present in the molecules of at least one of the compounds forming the nematogenic composition.

5. A composition according to any of the preceding claims, wherein the salt used is a quaternary ammonium and/or phosphonium salt.

6. A composition according to any of the preceding claims, wherein the nematogenic

composition comprises at least one isomeric pair and/or at least one eutectic mixture of compounds of the general formula: —



in which A has the same meaning as in claim 1 and R_1 and R_2, which may be the same or different, are alkyl, alkoxy or acyloxy radicals containing up to 18 carbon atoms.

7. A composition according to claim 6, wherein the substituents R_1 and R_2 contain up to 8 carbon atoms.

8. A composition according to any of the preceding claims, wherein the nematogenic composition comprises a eutectic mixture of 4 - (*n* - butyl) - 4′ - methoxy - azoxybenzene and 4 - ethyl - 4′ - methoxy - azoxybenzene.

9. A composition according to any of the preceding claims, wherein the nematogenic composition comprises a eutectic mixture of *p,p′* - di - (*n* - butyl) - *p′* - azoxybenzene and the isomer pair *p* - (*n* - butyl) - *p′* - methoxy - azoxybenzene.

10. A composition according to any of the preceding claims, wherein the carboxylic acid is *p* - (*p* - methoxy - phenylazoxy) - benzoic acid or *p* - (*p* - ethoxy - phenylazoxy) - benzoic acid.

11. A nematogenic composition according to claim 1, substantially as hereinbefore described and exemplified.

12. A process for the modification of a nematogenic composition or compound, wherein a known nematogenic composition or compound is mixed with 0.001 to 2% by weight of at least one carboxylic acid of the general formula given in claim 1 and/or with at least one salt thereof.

13. A process according to claim 12, wherein there is used 0.01 to 0.25% by weight of at least one carboxylic acid of the general formula given in claim 1 and/or at least one salt thereof.

14. A process according to claim 12 or 13, wherein the radical A of the carboxylic acid is also present in the nematogenic compound or at least one of the molecules forming the nematogenic composition.

15. A process according to any of claims 12 to 14, wherein the salt used is a quaternary ammonium and/or phosphonium salt.

16. A process according to any of claims 12 to 15, wherein the nematogenic composition to be modified comprises at least one isomeric pair and/or at least one eutectic mixture of compounds of the general formula given in claim 6.

17. A process according to any of claims 12 to 16, wherein the nematogenic composition to be modified comprises a eutectic mixture of 4 - (*n* - butyl) - 4′ - methoxy - azoxybenzene and 4 - ethyl - 4′ - methoxy - azoxybenzene.

18. A process according to any of claims 12 to 17, wherein the nematic phase comprises a eutectic mixture of *p,p′* - di - (*n* - butyl) - *p′* - azoxybenzene and the isomer pair *p* - (*n* - butyl) - *p′* - methoxy - azoxybenzene.

19. A process according to any of claims 12 to 18, wherein the carboxylic acid used is *p* - (*p* - methoxy - phenylazoxy) - benzoic acid or *p* - (*p* - ethoxy - phenylazoxy) - benzoic acid.

20. A process according to claim 12 for the modification of nematogenic compositions or compounds, substantially as hereinbefore described and exemplified.

21. A nematogenic composition whenever prepared by the process according to any of claims 12 to 20.

22. A display device whenever comprising a nematogenic composition according to any of claims 1 to 11 and 21.

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